

Tutorials 1 Thermodynamics 2, 2024/2025

Exercise 1

Consider a perfect gas of N CO₂-molecules, which therefore behaves according to the equipartition theorem. CO₂ is a linear molecule.

- How many translational and rotational degrees of freedom does the molecule as a whole have?
- Each degree of freedom of the molecule (translational, rotational, vibrational) in fact comes from the specific translations of the individual atoms in the molecule. What is the total number of degrees of freedom for a CO₂-molecule?
- What is therefore the number of vibrational degrees of freedom for a CO₂-molecule?
- Determine the internal energy U per mole for the gas at $T = 1000$ K.
- Determine the enthalpy H per mole for the gas at $T = 1000$ K.
- Determine the molar heat capacity c_V of the gas at $T = 2000$ K.
- Determine the molar heat capacity c_P of the gas at $T = 2000$ K.
According to the resource section of Atkins (table 2B.1, ed. 11 or 12) the molar heat capacity at constant pressure is given by $c_P(\text{CO}_2) = 44.22 + 8.79 \cdot 10^{-3}T - 8.62 \cdot 10^{-5}T^{-2} \text{ Jmol}^{-1}\text{K}^{-1}$.
Compare your value with the result from the resource section of Atkins.

Exercise 2

State functions.

A state function is a function $f(x, y, z, \dots)$ of independent variables x, y, z, \dots for which the function has an unambiguous value for each of the combinations of variables x, y, z, \dots . A function $f(x, y)$ of two independent variables is a state function if the following holds

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{or} \quad \left(\frac{\partial f}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_f \left(\frac{\partial y}{\partial f} \right)_x = -1.$$

Consider the function $g(x, y) = \ln(xy^2) - x^2y^3$.

- Examine if $g(x, y)$ is a state function.
- Write $dg(x, y)$ as a total differential, so as $dg(x, y) = g_x dx + g_y dy$ and find an expression for $g_x(x, y)$ and $g_y(x, y)$.
- Find a Maxwell relation between $g_x(x, y)$ and $g_y(x, y)$ and check that the Maxwell relation indeed holds.
- Finally, we calculate Δg between $(x, y) = (1, 2)$ and $(x, y) = (4, 3)$.
Because $g(x, y)$ is a state function Δg should be independent of the chosen integration path. Check this by integrating $dg(x, y)$ first at constant y and subsequently at constant x , and alternatively, first at constant x and subsequently at constant y , which should give the same result.
Hint: use the total differential of $g(x, y)$ for that and the expressions found for $g_x(x, y)$ and $g_y(x, y)$.

Exercise 3

- Write down the characteristic equations for dU , dH , dA and dG for an electrical cell as a closed system, by adding the additional electrical work term $E dq$, in which E is the EMF (electromotive force, or cell potential, or preferably: cell voltage) and dq is the transferred electric charge.
- Determine all Maxwell-relations that you can derive from these equations.
- Determine the characteristic equations for dU , dH , dA and dG for an electrical cell as an open system, by adding also the term μdn . Assume that there is only one type of compound present in the cell.
- Determine all the Maxwell-relations that you can derive from the resulting equation for the Gibbs free energy.

Exercise 4

In this exercise we will use a Maxwell equation to rewrite the internal pressure (the isothermal volume dependence of the internal energy) expression, $\Pi_T \equiv \left(\frac{\partial U}{\partial V}\right)_T$ to $\Pi_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$. This latter equation allows to determine Π_T for gases from relatively easily measurable properties of the system.

- Show that for a perfect (molecular or atomic) gas, for which we have an expression for the internal energy U , that $\Pi_T = 0$.

For a (molecular or atomic) van der Waals gas, the equation of state keeps track of the finite size of the atoms or molecules in the gas as well as of the attraction between the particles:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2},$$

where a and b are coefficients characteristic for the gas involved, which respectively account for the attraction and repulsion of the molecules in a non-perfect gas.

- To find the alternative expression for Π_T mentioned above, first show that we can write

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial V}{\partial V}\right)_T,$$

using the total differential of $U(S, V)$.

- Next, use the characteristic equation for $U(S, V)$ and a Maxwell relation to get rid of the partial derivative $\left(\frac{\partial S}{\partial V}\right)_T$, to rewrite the result of b) to the expression for Π_T we were looking for.
- Apply this expression to CO_2 as a non-perfect van der Waals gas, for which $a = 3.610 \text{ atm dm}^6 \text{ mol}^{-2}$ and $b = 4.29 \cdot 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$.

Use the result to determine the change in internal energy ΔU (in J) for an isothermal compression of 2 mol of the gas from 400 dm^3 to 200 dm^3 at $T = 2000 \text{ K}$.

Advice: always convert data to SI-units; $1 \text{ atm} = 1.01325 \cdot 10^5 \text{ Pa} = 1.01325 \cdot 10^5 \text{ N/m}^2$.